

423/240 S

(7)

PATENT SPECIFICATION

NO DRAWINGS

1.046.313

1.046.313



Date of Application and filing Complete Specification April 21, 1965.

No. 16776/65.

Application made in Netherlands (No. 6404460) on April 23, 1964.

Complete Specification Published: Oct. 19, 1966.

© Crown Copyright 1966.

GT. BRIT.

DIV.

Index at acceptance:—Cl A(K3B, K3C, K3D)

Int. Cl.:—C 01 b 7/00

COMPLETE SPECIFICATION

Process for the Preparation of Chlorine, Bromine or Iodine
and for the Preparation of Halogenated Hydrocarbons

We, SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ N.V., a Company organised
under the laws of the Netherlands of 30
Carel van Bylandtlaan, The Hague, Holland,
do hereby declare the invention, for which
we pray that a patent may be granted to us,
and the method by which it is to be per-
formed, to be particularly described in and
by the following statement:—

The invention relates to the preparation of
chlorine, bromine or iodine from the com-
pounds of these halogens with hydrogen. The
invention is of particular importance to the
preparation of chlorine from hydrogen chlori-
de. The invention also relates to the prepara-
tion of halogenated hydrocarbons.

A known technique to prepare halogens
from hydrogen halide compounds is to bring
the latter compounds, mixed with oxygen or
a free oxygen-containing gas, into contact
with a catalyst. In the traditional Deacon
process copper compounds were used as a
catalyst. Compounds of other metals have
since also been suggested as catalysts for this
oxidation. In general, the conversion percent-
ages in these known processes are appreciably
lower than would correspond with the equi-
librium. Not until recently were improvements
brought about by the application of combina-
tions of compounds of copper, rare earth
metals and alkali metals.

It has now been found that in the oxida-
tion of hydrogen chloride, hydrogen bromide
or hydrogen iodide in the gaseous phase,
ruthenium compounds are very effective cata-
lysts. With these catalysts the equilibrium can
be reached at relatively low temperatures.

The invention can be defined as relating to
the preparation of chlorine, bromine and/or
iodine from the corresponding hydrogen
halides, in which a gaseous mixture containing
hydrogen halide and oxygen is brought into

contact with a catalyst containing at least
one ruthenium compound.

A very suitable ruthenium compound is
ruthenium trichloride. In the oxidation of
hydrogen chloride temperatures between 250
and 500°C may be used. Especially suitable
are temperatures between 325 and 400°C, but
the process can quite well be carried out
above 400°C.

In the process according to the invention
atmospheric pressures have proved very satis-
factory. A pressure increase results in a shift
of the equilibrium towards halogen and water
and may therefore be favourable. Although in
general the operating pressure will not be out-
side the range of 1 to 5 atm abs., the reaction
may in principle proceed at either higher or
lower pressures, for example, between 0.1 and
100 atm abs.

The ruthenium compounds are preferably
applied on a carrier. The usual carriers have
given good satisfaction. Examples of suitable
carriers are silica gel, aluminium oxide,
pumice and ceramic materials. The amount
of ruthenium in the catalyst is as a rule be-
tween 0.1 and 15% by weight, calculated as
metal compound on the sum of metal com-
pound and carrier.

The present catalysts may be applied in
both fixed beds and fluidized beds.

The oxidation takes place by means of
gaseous oxygen. Usually, the gaseous hydro-
gen halide is mixed with air. Besides air, how-
ever, other free oxygen-containing gases as
well as pure oxygen may in principle also be
used.

The ratio of hydrogen halide to oxygen
may certainly be the stoichiometric one. If
desired, however, one may depart from the
stoichiometric ratio and pass mixtures over
the catalyst in which the ratio of hydrogen
halide to oxygen is between five times the
stoichiometric ratio of one fifth of this ratio.

The catalyst is supported on a carrier in a conventional manner. A very suitable process is one in which the carrier is mixed with such a quantity of a solution of a ruthenium compound in water as can just be absorbed by the carrier material. In this way the catalyst is distributed uniformly over the carrier, while no remaining solution need be separated. The concentration of the solution is chosen such as to obtain the desired ratio of ruthenium to carrier.

The gaseous mixture used as the starting material may also contain one or more hydrocarbons, in which case these hydrocarbons enter into reaction with the halogen formed. In

this manner halogen can be added to unsaturated aliphatic hydrocarbons and halogen can be substituted for hydrogen atoms in saturated aliphatic or cycloaliphatic hydrocarbons as well as in aromatic hydrocarbons. In these cases high conversions of hydrogen halide are as a rule attained even at temperatures that are appreciably lower than in the absence of hydrocarbons. Suitable temperatures are frequently between 100 and 300°C.

EXAMPLE

Preparation of the catalyst

As carrier silica was used with the following properties:

surface area	- - - - -	292	m ² /g
pore volume	- - - - -	0.67	ml/g
average pore diameter	- -	91.4	Å
sodium content	- - - - -	0.13	%
iron content	- - - - -	0.11	%

The carrier was dried for two hours at 500°C and subsequently soaked in a solution of ruthenium trichloride. The impregnated carrier was dried at 100°C and finally heated for three hours in an air stream at 250°C.

The concentration of the solution of the ruthenium trichloride was varied in various experiments to obtain catalysts with different ruthenium contents. The ruthenium contents were calculated as per cent by weight of metal on the sum of metal and carrier.

Preparation of chlorine

Hydrogen chloride gas and air were passed over the catalyst at atmospheric pressure, in a stoichiometric ratio and at a rate of 60 litres HCl per kg catalyst and per hour. The percentage of ruthenium in the catalyst and the temperature were varied.

The table below gives the conversion percentages and, for comparison, the equilibria.

TABLE

% Ru	Temperature °C		
	300	325	350
5.00	—	40	56
8.21	44	66	76
12.91	46	67	79
equilibrium	85	82	79.5

WHAT WE CLAIM IS:—

1. A process for the preparation of chlorine, bromine and/or iodine from the corresponding hydrogen halides, in which a gaseous mixture containing hydrogen halide and oxygen is brought into contact with a catalyst containing at least one ruthenium compound.

2. A process as claimed in claim 1, in

which the ruthenium compound is ruthenium trichloride.

3. A process as claimed in claim 1 or 2, in which the temperature is between 250 and 500°C.

4. A process as claimed in claim 3, characterized in that the temperature is between 325 and 400°C.

5. A process as claimed in any of the preceding claims, in which a pressure between 0.1 and 100 atmospheres is applied.

6. A process as claimed in claim 5, in which the pressure is between 1 and 5 atmospheres.

7. A process as claimed in any of the preceding claims, in which the ruthenium compound is supported on a carrier.

8. A process as claimed in claim 7, in which the amount of ruthenium in the catalyst is between 0.1 and 15% by weight, calculated as metal compound on the sum of metal compound and carrier.

9. A process as claimed in any of the preceding claims, in which the ratio of hydrogen halide to oxygen is between five times the stoichiometric ratio and one fifth of this ratio.

10. A process as claimed in any of the preceding claims in which the gaseous mixture which is taken as starting material also contains one or more hydrocarbons.

11. A process substantially as described in the Example.

12. A halogen whenever prepared according to any of the preceding claims.

13. A process for the preparation of halogenated hydrocarbons wherein hydrocarbons are reacted with halogen, characterized in that the reaction is performed in a gaseous mixture as claimed in claim 10.

14. A process as claimed in claim 13, characterized in that the temperature is between 100 and 300°C.

5 15. Halogenated hydrocarbons prepared according to claim 13 or 14.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings,
Chancery Lane,
London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

805/68 Prod. of Cl₂, Br₂, or I₂ from corres-
ponding hydrogen halide, using as a catalyst one or
more ruthenium compound(s). 21.4.65.
(23.4.64. Neth. as 6404460) SHELL INT. RES.
MIJ NV (12.1.68) 14F.